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RADIOLYTIC INSTABILITY OF FERROUS SULFAMATE IN  
NUCLEAR PROCESS SOLUTIONS

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Ned E. Bibler (PhD, radiation chemistry, Ohio State University, 1965) is presently a staff chemist in the Separations Chemistry Division at the Savannah River Laboratory. His interests are in the chemical effects of radiation associated with nuclear fuel reprocessing, with separating and purifying intensity radioactive sources such as  $^{244}\text{Cm}$  and  $^{238}\text{Pu}$ , and with storing radioactive wastes. He has performed basic radiolysis studies with  $^{60}\text{Co}$   $\gamma$ -rays,  $^{244}\text{Cm}$   $\alpha$ -particles, and  $^{252}\text{Cf}$  fission fragments.

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## ABSTRACT

The radiolytic oxidation of Fe(II) and destruction of sulfamic acid (SA) in feed solutions for solvent extraction purification of  $^{237}\text{Np}$  and  $^{238}\text{Pu}$  from spent nuclear fuels have been investigated.  $^{60}\text{Co}$   $\gamma$ -radiolysis of simulated solutions established that 100-eV yields for depletion of Fe(II) and SA are 13 and 5.6, respectively. Also, the normally occurring components of process solutions do not significantly affect these yields. An actual process solution was studied in which radiolysis was almost entirely from  $\gamma$ - and  $\beta$ -decay of  $^{235}\text{U}$  fission products along with a small fraction from  $\alpha$ -decay of transuranium isotopes. In this solution,  $G(\text{Fe}^{3+})$  is 12, which is in good agreement with results with simulated solutions. Interpretation of the results suggests that Fe(II) not only reduces Np(V) and Pu(IV), but also protects the reduced states from reoxidation by radiolytically formed intermediates; when Fe(II) is depleted, the reduced states are immediately oxidized.

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### INTRODUCTION

Many processes for separation and purification of Np and Pu from irradiated U fuels depend upon  $\text{Fe}(\text{SA})_2$  (ferrous sulfamate) as a reductant.<sup>1</sup> Np and Pu in the solutions resulting from  $\text{HNO}_3$  dissolution of spent reactor fuel exist primarily as Np(V) and Pu(IV). These elements can be separated by solvent extraction<sup>2</sup> or ion exchange<sup>3</sup> after they are reduced to Np(IV) and Pu(III) by Fe(II). For example, in one modification of the Purex solvent extraction process,<sup>2</sup> ferrous sulfamate is added to the feed to reduce Np(V) to Np(IV) and Pu(IV) to Pu(III). Sulfamate is added to prevent  $\text{NO}_3^-$  oxidation of Fe(II), which is catalyzed by traces of  $\text{HNO}_2$  produced thermally or radiolytically.<sup>4</sup> Np(IV) is extracted into the organic solvent (3.5% TBP in a hydrocarbon solvent), and Pu(III) remains in the aqueous phase. If Pu(III) is oxidized during the process, it is also extracted; if Np(IV) is oxidized, it is not extracted. Both of these lead to incomplete separations. It has been found in practice that the reductant Fe(II) must be present during the complete process because it apparently by some mechanism stabilizes the reduced states of both elements.<sup>5</sup>

These process solutions are radioactive from  $^{235}\text{U}$  fission products, and also from transuranium isotopes formed by neutron absorption; therefore oxidizing agents such as  $\text{H}_2\text{O}_2$  and OH radicals are continuously being formed from radiolysis of the water. These

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can easily deplete the Fe(II) concentration by oxidation. Such oxidation has been observed in radiolysis of dilute  $\text{NO}_3^-$  solutions<sup>6</sup> and of  $\text{H}_2\text{SO}_4$  solutions where it serves as basis for the Fricke Dosimeter.<sup>7</sup>

This article reports results of a study of radiolytic Fe(II) oxidation in concentrated  $\text{NO}_3^-$  solutions used for solvent extraction separation of Np and Pu.<sup>2</sup> In addition to  $^{60}\text{Co}$  irradiations of simulated solutions, the effect of radiolysis on the stabilities of Fe(II), Np(IV), and Pu(III) was determined in an actual radioactive process solution.

### EXPERIMENTAL PROCEDURE

All reagents were research grade and used without further purification. Solutions were prepared in triply distilled water. Ferrous sulfamate solution was prepared by dissolving iron filings with sulfamic acid. The final solution had a slight excess of sulfamate. Simulated process solutions (2.0M  $\text{HNO}_3$ , 1.5M  $\text{Al}(\text{NO}_3)_3$ , 0.03M  $\text{UO}_2^{2+}$ , 0.02M  $\text{Hg}^{2+}$ , and 0.02M  $\text{Mn}^{2+}$ ) were irradiated with a Gammacell 220  $^{60}\text{Co}$  source\* at ambient temperature (30-37°C). Source intensity was determined with the Fricke Dosimeter,<sup>7</sup> and dose to irradiated solutions was calculated by the ratio of electron densities of the respective solutions. The dose rate was  $6.09 \times 10^5$  rads/hr. Fe(II)

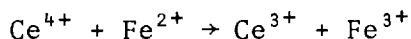
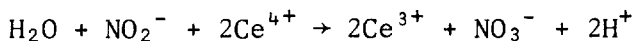
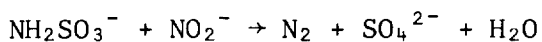
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concentrations were determined by titration with standard Ce(IV) solution. Test indicated that none of the radiolytic products interfered with this analysis. Sulfamate concentrations were determined by addition of excess standard  $\text{NO}_2^-$  at the equivalence point in the Fe(II) determination, followed by an excess of standard Ce(IV) solution. The sulfamate concentration was then determined from the amount of standard Fe(II) solution necessary to titrate unreacted Ce(IV).

The chemical reactions pertinent to this analysis are:



Accuracy of the method was established by analyzing sulfamate solutions that had been standardized by NaOH titration.

Experiments with a radioactive process solution resulting from dissolution of irradiated  $^{235}\text{U}$  fuel tubes were performed remotely in a shielded facility.  $\text{Fe}(\text{SA}_2)$  was added to the solution, and Fe(II) concentration was determined as a function of time by potentiometric titration of a small aliquot of the solution with standard Ce(IV) solution. For the titration, the aliquot was diluted so that the radiation field in the solution did not affect the analysis by inducing reduction of Ce(IV). The redox potential ( $E_h$ ) relative to the normal hydrogen electrode was measured with Pt and calomel electrodes. At various times

aliquots of the solution were contacted with thenoyltrifluoroacetone (TTA) at such conditions that Pu(IV) and Np(IV) were extracted and Pu(III) and Np(V) remained in the aqueous phase. Determination of  $^{238}\text{Pu}$  and  $^{237}\text{Np}$   $\alpha$  activity in the organic phase allowed calculation of the percent of each isotope that remained in the lower oxidation states. Dose rate in the solution was calculated from the  $\alpha$ ,  $\beta$ , and  $\gamma$  radiation absorbed by the solution and the average energy of each type of radiation.  $\alpha$  and  $\beta$  rates were determined by proportional counting;  $\gamma$ , by scintillation pulse height analysis.  $\beta$  and  $\gamma$  energies for the  $^{235}\text{U}$  fission products were calculated with a computer code that determines the activities and average energies of these fission products as a function of reactor irradiation time and isotope decay time.<sup>8</sup> For this specific solution, the calculated average  $\beta$ - and  $\gamma$ -decay energies were 0.37 and 0.64 MeV, respectively.  $\alpha$  particles were from  $^{238}\text{Pu}$  ( $E_{\text{av}} = 5.5$  MeV) and  $^{239}\text{Pu}$  ( $E_{\text{av}} = 5.2$  MeV).

## RESULTS AND DISCUSSION

Depletion of Fe(II) and SA concentrations during  $\gamma$ -radiolysis of a simulated process solution is shown in Figure 1. Less than 5% of the Fe(II) oxidation during the total irradiation time was due to nonradiolytic processes, as calculated from the rate constant for first order thermal oxidation of Fe(II) ( $k = 0.035 \text{ hr}^{-1}$  at  $35^\circ\text{C}$ ).<sup>9</sup> This was confirmed by analysis of an unirradiated solution after 2 hr. From slopes determined by least squares analysis of Figure 1,



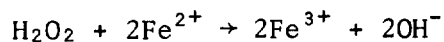
the G values for the depletion of Fe(II) and SA are 13 ions/100 eV and 5.6 molecules/100 eV, respectively.

Linearity of the data for Fe(II) depletion over the entire dose range studied indicated the absence of any radiolytic reactions leading to the reduction of Fe(III) in this system. Also, linearity for sulfamate depletion indicated that the reactions leading to its destruction are not influenced by the presence of Fe(II). This suggests that the radiolytic intermediates that oxidize Fe(II) do not decompose sulfamate in these solutions.

To determine the effect of the major components of the process solutions ( $\text{Al}^{3+}$ ,  $\text{NO}_3^-$ ,  $\text{H}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{UO}_2^{2+}$ ) on  $G(\text{Fe}^{3+})$ , 12 experiments based on a Plackett-Burman screening design<sup>10</sup> were performed. Mathematical analysis<sup>10</sup> of the effect of these ions on  $G(\text{Fe}^{3+})$  indicated that within the nominal concentration limits of the respective components, only  $\text{NO}_3^-$  significantly affected  $G(\text{Fe}^{3+})$ . When  $\text{NO}_3^-$  was lowered to 0.5M,  $G(\text{Fe}^{3+})$  decreased to 9.6 ions/100 eV. This indicates that the primary water radiolysis products are not the only reactive species oxidizing Fe(II). Perhaps some  $\text{NO}_x$  species formed by direct radiolysis of  $\text{NO}_3^-$  also oxidizes Fe(II). Also, saturation of the solution with organic extractant (tributyl phosphate in a hydrocarbon diluent) during radiolysis did not affect  $G(\text{Fe}^{3+})$ . This is in contrast to the Fricke Dosimeter where organics increase the oxidation of Fe(II).

Figure 2 shows the decrease in Fe(II) concentration in a process solvent extraction feed solution containing  $^{235}\text{U}$ , fission products,  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$ ,  $^{238}\text{Pu}$ , and traces of other transuranium isotopes. Solution composition was 1.5M  $\text{HNO}_3$ , 1.6M  $\text{Al}(\text{NO}_3)_3$ , 0.019M  $\text{UO}_2^{2+}$ ,  $\sim 10^{-5}\text{M}$   $^{239}\text{Pu}$ ,  $\sim 10^{-5}\text{M}$   $^{237}\text{Np}$ ,  $\sim 10^{-2}\text{M}$   $\text{Hg}^{2+}$ , and  $10^{-2}\text{M}$   $\text{Mn}^{2+}$ . Calculations indicated that only  $\sim 7\%$  of the total Fe(II) depletion is due to nonradiolytic thermal processes ( $k = 0.009\text{ hr}^{-1}$  at  $25^\circ\text{C}$ ).<sup>9</sup> The initial Fe(II) concentration as determined by extrapolation in Figure 2 agreed within 2% of that calculated from the amount added, indicating that significant amounts of oxidizing agents such as  $\text{H}_2\text{O}_2$  or  $\text{NO}_2^-$  did not accumulate in process solutions from self-radiolysis.

Figure 3 shows the redox potential of the solution and the percent of Np or Pu in the 4+ state as a function of time. Before addition of  $\text{Fe}(\text{SA})_2$ , the measured potential was 1.06 V, and no Pu(III) or Np(IV) was present. After addition of  $\text{Fe}(\text{SA})_2$ , the potential decreased and all the Np(V) and Pu(IV) were rapidly reduced. This potential is controlled primarily by the Fe(II)-Fe(III) couple. After complete oxidation of Fe(II) ( $\sim 8\text{ hr}$ ), the potential increased rapidly to nearly its original value, and Np(IV) and Pu(III) were quickly oxidized. Apparently, Fe(II) not only reduces Np(V) and Pu(IV), but also protects the reduced states by scavenging the radiolytically produced oxidizing species, OH and  $\text{H}_2\text{O}_2$ .



After Fe(II) is consumed, OH radicals and H<sub>2</sub>O<sub>2</sub> rapidly oxidize the Pu(III) and Np(IV). This protective action accounts for the stabilizing effect of Fe(II) detected earlier.<sup>5</sup> Apparently sulfamate does not act as a protective reagent because, even though it is still present after complete oxidation of the Fe(II) (as indicated by the data in Figure 1), Pu(III) and Np(IV) are still rapidly oxidized. The behavior of the redox potential suggests that this parameter could be used as a process monitor to determine the presence of Fe(II) and thus indicate whether Np and Pu are reduced. Further development work would be necessary though for this application.

The dose rate to this solution from the <sup>235</sup>U fission products and the α-emitting transuranium isotopes was then calculated to determine G(Fe<sup>3+</sup>) for comparison to that determined from radiolysis of a simulated solution. Data for this calculation are shown in Table I. The solution volume was ~50 ml occupying a 4.5-cm-diameter cylinder, 3 cm tall. The ranges of the α and β particles<sup>11</sup> are so small that α and β energy is 100% absorbed by the solution. The fraction of γ-ray energy absorbed was determined as follows: the fraction transmitted from the solution was assumed equal to that transmitted from a sphere with a surface-to-volume ratio identical to that of the cylinder occupied by the solution.<sup>12</sup> A

value of  $0.033 \text{ cm}^{-1}$  was used for the linear energy absorption coefficient for the  $\gamma$ -rays with an average energy of 0.64 MeV.<sup>13</sup> The energy absorbed is then the product of: one minus the fraction transmitted; intensity of the  $\gamma$ -rays; and their average energies. Because the  $\gamma$ -dose rate is only a small part of the total, errors in estimating the percent of  $\gamma$ -ray energy absorbed do not significantly affect the value for  $G(\text{Fe}^{3+})$ . As shown in Table I,  $\gamma$ - and  $\beta$ -decay of fission products account for >99% of the radiolysis of the solution, and  $\alpha$ -decay of transuranium isotopes accounts for only ~0.5%. With a total dose rate of  $1.5 \times 10^5$  rads/hr and the least squares slope of Figure 2,  $G(\text{Fe}^{3+})$  is 12, which is in excellent agreement with that determined from  $\gamma$ -radiolysis of simulated process solutions. This indicates that the time dependence of Fe(II) concentration in radioactive process solutions can be successfully calculated from the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -disintegration rates of the dissolved isotopes, their average decay energies, and the fraction of radiation absorbed.

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TABLE I

Dose rate from  $^{235}\text{U}$  fission products and  
transuranium isotopes dissolved in a nuclear process solution

<u>Radiation</u>	<u>Activity</u> <u>[d/(min)(ml)]</u>	<u>Average</u> <u>energy (MeV)</u>	<u>Percent</u> <u>absorbed</u>	<u>Dose rate</u> <u>(<math>10^5</math> rads/hr)</u>
$\alpha$	$1.8 \times 10^8$	5.5	100	0.008
$\beta$	$4.9 \times 10^{11}$	$0.37^a$	100	1.45
$\gamma$	$2.0 \times 10^{11}$	$0.64^a$	4	0.04

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$a$ . Calculated from PHOEBE Code.<sup>8</sup>

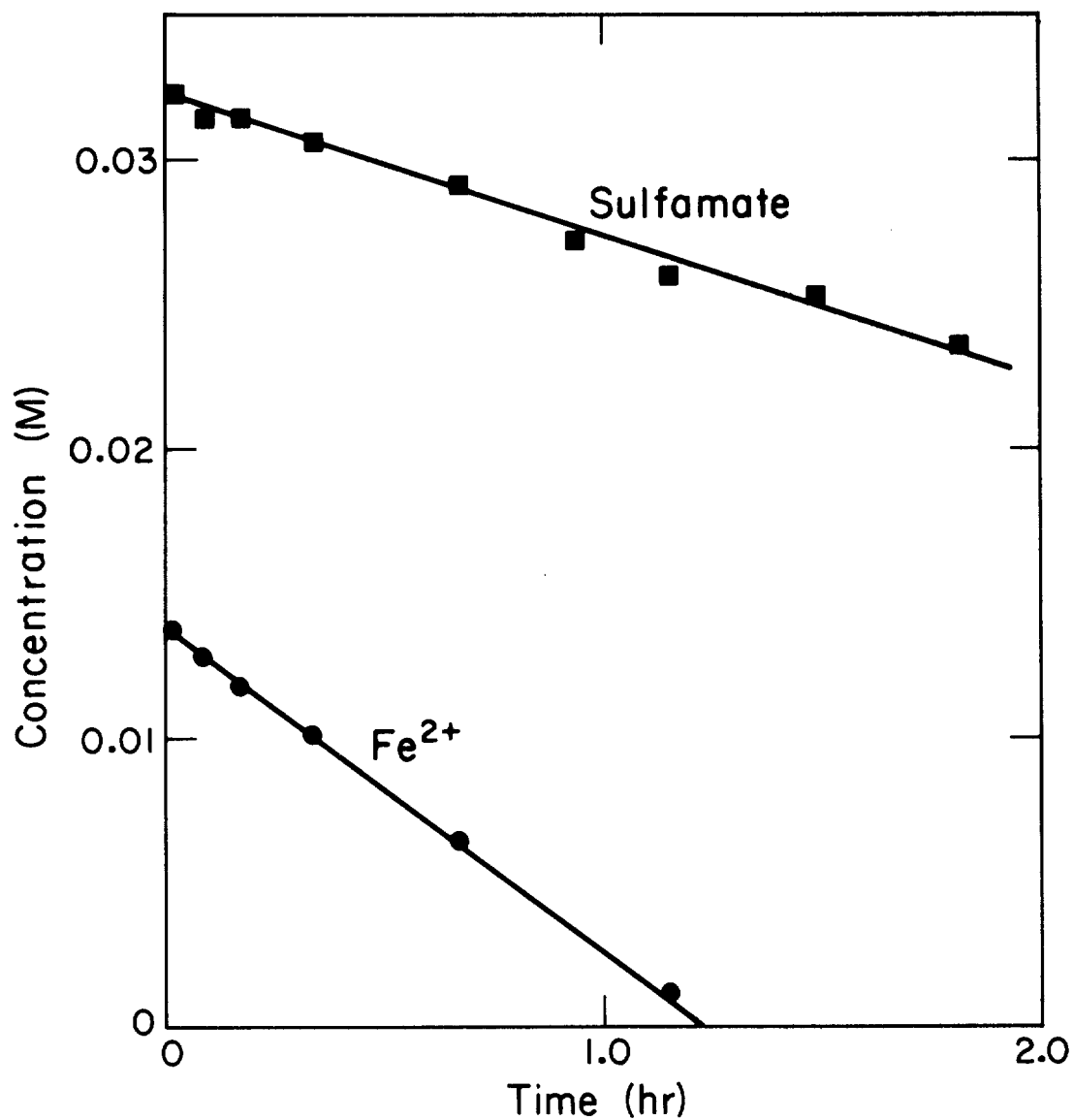


FIGURE 1. Depletion of Fe(II) and sulfamate from  $^{60}\text{Co}$   $\gamma$ -radiolysis of simulated process solutions.

Dose rate =  $6.09 \times 10^5$  rads/hr,  $T = 30\text{--}37^\circ\text{C}$ .

● Fe(II), ■ Sulfamate



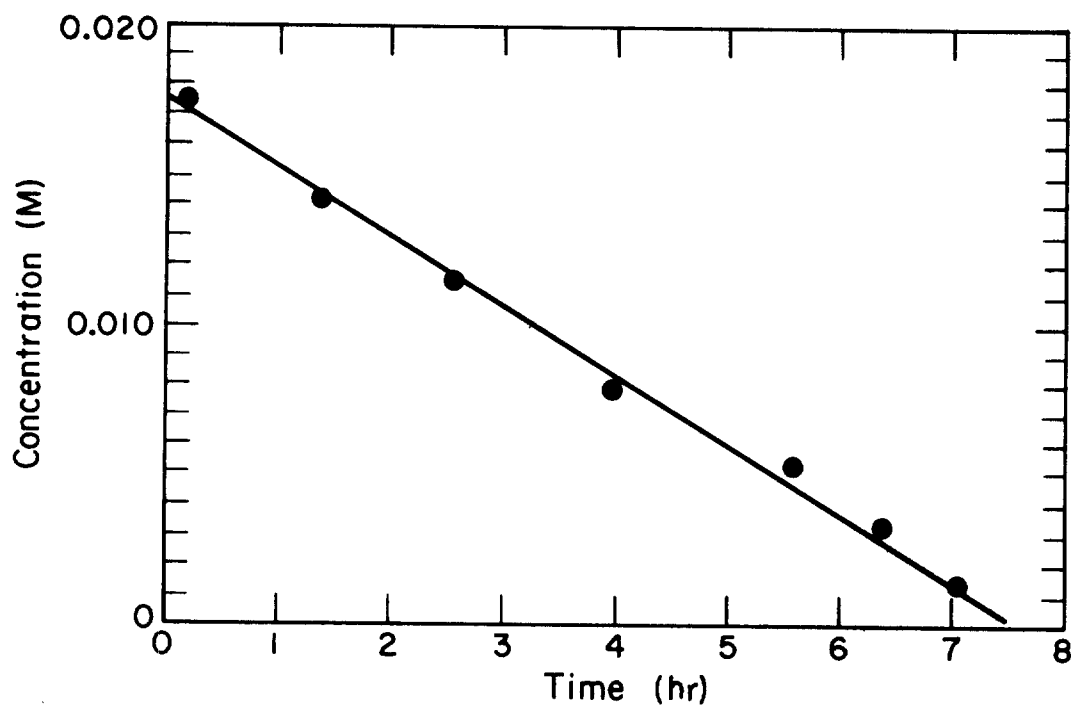


FIGURE 2. Depletion of Fe(II) from radiolysis by dissolved fission products of  $^{235}\text{U}$  in actual process solution. Dose rate =  $1.5 \times 10^5$  rads/hr,  $T = \sim 25^\circ\text{C}$ .

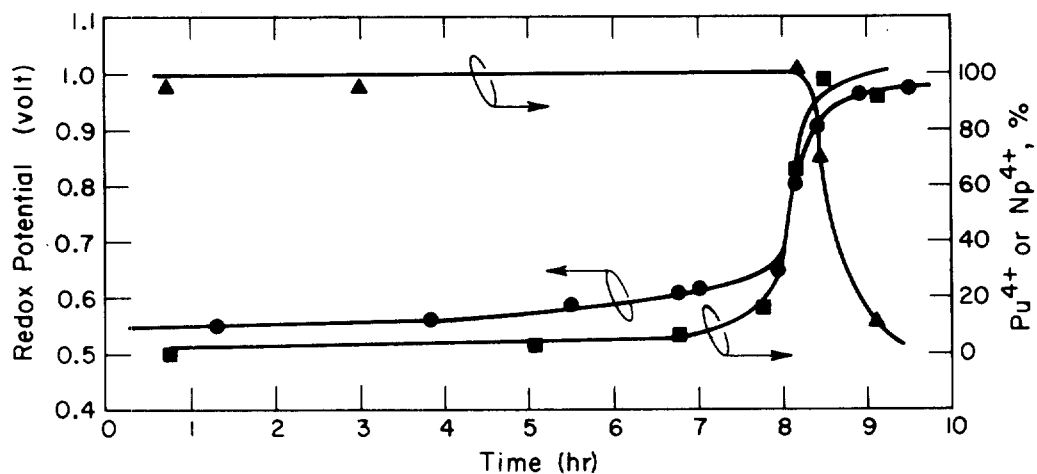


FIGURE 3. Dependence of the redox potential and fraction of  $^{237}\text{Np}$  or  $^{238}\text{Pu}$  in the 4+ state on radiolysis by dissolved fission products of  $^{235}\text{U}$  in an actual process solution. Dose rate =  $1.5 \times 10^5$  rads/hr,  $T = \sim 25^\circ\text{C}$ .

● Redox Potential, ■ Percent Pu(IV), ▲ Percent Np(IV)

LEGENDS FOR FIGURES

FIGURE 1. Depletion of Fe(II) and sulfamate from  $^{60}\text{Co}$   $\gamma$ -radiolysis of simulated process solutions.

Dose rate =  $6.09 \times 10^5$  rads/hr, T = 30-37°C.

● Fe(II), ■ Sulfamate

FIGURE 2. Depletion of Fe(II) from radiolysis by dissolved fission products of  $^{235}\text{U}$  in actual process solution.

Dose rate =  $1.5 \times 10^5$  rads/hr, T = ~25°C.

FIGURE 3. Dependence of the redox potential and fraction of  $^{237}\text{Np}$  or  $^{238}\text{Pu}$  in the 4+ state on radiolysis by dissolved fission products of  $^{235}\text{U}$  in an actual process solution.

Dose rate =  $1.5 \times 10^5$  rads/hr, T = ~25°C.

● Redox Potential, ■ Percent Pu(IV), ▲ Percent Np(IV)